PATENT SPECIFICATION (11) 1 213 333

NO DRAWINGS

1 213 333

(21) Application No. 43926/68 (22) Filed 16 Sept. 1968
(45) Complete Specification published 25 Nov. 1970
(51) International Classification C 11 d 9/02 9/46
(52) Index at acceptance
C5D 6B12B1 6B12B2 6B12E 6B12F1 6B12F2 6B12G2A 6B12G6 6B12M 6B12N1 6B12N2 6B12N5 6C9
(72) Inventors TOMOO ITO
MICHITARO KAWAGUCHI
FRANKLIN CONRAD

(54) A COMPOSITION FOR USE IN THE MANUFACTURE OF SOAP

(71) We, ETHYL CORPORATION, a corporation organised under the laws of the State of Virginia, United States of America, of 330, South Fourth Street, Richmond, State of Virginia, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a composition comprising a mixture of carboxylic acids which may be converted to metallic soaps useful as cleaning materials in, for example, hand soaps, laundry soaps or dishwashing soaps. More particularly, the invention relates to soap compositions having improved stability against deterioration, achieved by materially lowering or eliminating conventional unsaturation or unsaturated molecules, particularly that of the conjugated or polyunsaturated type, and employing soap components derived from higher fatty acids having branched chain carbon skeletal configurations to provide a desired titre (low melting point).

Conventional soap, the main constituents of which are natural source (ester) derived fatty acid salts, are prepared fundamentally from tallow and coconut oil systems, or other oils and fats, or derivatives of such materials. Typical proportions are 20 percent coconut oil fatty acids and 80 percent tallow fatty acids. Tallow fatty acids are generally about 40 to 50 percent oleic acid, 6 percent polyunsaturated acids, with the balance C_{14} to C_{18} saturated acids. The composition of the raw material oils or the mixed fatty acids is carefully controlled to impart desired properties to the product soaps and also to provide materials having desirable processing properties.

The principal aforementioned properties are plasticity, density, solubility, foamability and detergency. Plasticity relates more to the processing of the products whilst the remaining properties relate more to the use of the products. It is possible to select fatty acid mixtures and vary the proportions to provide desired properties for the mass, but one desired property relate to the plasticity of soaps, namely that of a low melting point (titre) for the materials, as acid mixtures, creates a problem. Conceivably, the lower straight chain saturated fatty acids could impart desirable characteristics of this nature but their use is not favoured in many instances because of skin irritation considerations. Thus, low cost unsaturated fatty acids of tallow source or the equivalent are generally considered to be essential components of the fatty acid constituents used to make soaps, the tallow fatty acids playing an important role in adjusting plasticity and solubility. In general, reference is made to an "acid" titer for defining characteristics of soap raw materials, even where the materials as actually used are in other forms such as esters. Thus, when reference is made to a titre in connection with esters, it is with reference to mixtures whose acid components, as acids, have a specified titre.

Unfortunately, conjugated or polyunsaturated acids are so chemically unstable that they cause rancidity of the soaps. Certain additives, such as skin emollients, antioxidants and chelating agents, can be used to inhibit rancidity, but any improvements due to such materials are usually quite minor and are generally of a "masking" nature rather than being really effective.

The mixed fatty acids composition which shows a titre of 35 to 40°C is considered to be desirable for solid soaps, more specifically toilet soaps. With known soap compositions generally, a preferred unsaturated fatty acid content can be about 35 percent by weight, but somewhat higher percentages are usually acceptable. When the unsatur-

[*Price 5s. 0d. (25p)*]

ated fatty acid content is increased much above 35 percent by weight, however, the stability of the soap product is reduced and the soap becomes soft, while the foams produced by the soap becomes undesirably fine and viscous. When the unsaturated fatty acid content is decreased much below 35 percent by weight, the properties of stability, firmness and foam quality may be improved somewhat, but the plasticity is reduced thereby making the processing leading to the formation of bars more difficult. When the unsaturated fatty acid content is as low as 30 percent or less, the plasticity and other factors are reduced so significantly that the mouldability of the soap into bars is significantly impaired.

As a result of a study on the properties of salts of higher branched chain carboxylic acids obtained either directly by the reaction of a straight chain olefin as a starting material with carbon monoxide and water, or by oxidation of a higher oxo alcohol obtained from a straight chain olefin, we have found that solid soap having high foamability, detergency, plasticity and stability can be obtained by employing mixtures based on saturated fatty acids having both branched chains and straight chains obtained from natural oils or fats, from fatty acids which consist mostly of saturated acids obtained from hydrogenated fats or oils, or from synthetic sources.

Further, we have found that, maintaining other properties, the stability of soap products can be improved remarkably without reducing the quickness of foaming or the plasticity by replacing at least a part of the unsaturated fatty acids in the fatty acid compositions corresponding to known conventional formulations (for example, 75 percent tallow and 25 percent coconut oil) with the above mentioned branched chain saturated fatty acid.

Accordingly the present invention provides a composition for use in the manufacture of soap, which composition comprises a major amount of a mixture consisting of a major amount of an acid or acids having the formula

$$\text{II} \quad C_aH_{2a+1} - CH_2 - COOH$$

wherein a is an integer of from 9 to 20, and a minor amount of an acid or acids having the formula

$$\text{I} \quad C_nH_{2n+1} - \underset{\displaystyle C_mH_{2m+1}}{\underset{|}{CH}} - COOH$$

wherein n is an integer equal to or greater than 1, m is an integer equal to or greater than n, and the sum of m and n is greater than 8 but less than 25, the titre (melting point) of the mixture being from 35°C to 40°C.

The acid of Formula I is preferably a saturated α-methyl, α-ethyl, α-propyl or α-butyl acid, either pure or as a mixture. Examples of such acids are α-substituted caproic, enanthic, caprylic, pelargonic, capric, undecanoic, lauric, tridecanic, myristic, pentadecanoic, palmitic, margaric, stearic, nonadecanoic and arachidic acid. The sum of m and n is preferably greater than 10 but less than 19.

The acid of Formula II is preferably in the coconut range of normal acids, having from 8 to 16 carbon atoms per molecule, or stearic acid (C_{18}), usually obtained from tallow. It is also preferred that the acid or acids of Formula II be present in an amount of up to 85 percent by weight of the mixture.

The titre of the materials of the mixtures, as acids, is from 35° to 40°C.

As to the titres of branched fatty acids, an acid having a methyl radical in the α-position shows a comparatively higher titre, whereas when the side chain in the α-position is longer the titre is comparable to oleic acid, whose melting point is 14°C. For C_3 and above, variation of the the length of the branch chain for a given number of total carbon atoms per molecule does not appreciably affect the titre.

Titres of Typical Branched Chain Saturated Fatty Acids	
α-methyl undecanoic, C_{12}	18°C
α-ethyl capric, C_{12}	5°C
α-butyl caprylic, C_{12}	3°C
α-methyl tridecanoic, C_{14}	34°C
α-methyl pentadecanoic, C_{16}	43°C
α-methyl margaric, C_{18}	54°C

When the acid of Formula I is mixed with that of Formula II, one or more acids of Formula I having proper titres may be used.

Preferably at least 15 percent of the acid or acids of Formula I are used. When an acid or acids of Formula I having a titre corresponding approximately to that of oleic acid are employed in an amount of less than 30 percent, a favourable plasticity is obtained. In order to make solid soap with the acids of Formula I and II it is desirable to use 20 to 70 parts, preferably 30 to 60 parts and typically 30, 40, 50 or 60 parts, of the acid of Formula I with 100 parts of the acid of Formula II. On a percentage basis this may be described as broadly from 15 to 40 percent by weight of acid of Formula I, preferably from 25 to 30 percent by weight. In a system of straight chain unsaturated acids, in which oleic acid is predominant, and acids of Formula II where the unsaturated acids are replaced at least in part, more preferably wholly, with acids of Formula I, it is desirable that the total amount of the

acids of Formula I and the straight chain unsaturated acids be from 30 to 80 parts by weight, preferably from 50 to 70 parts by weight against 100 parts by weight of the acids of Formula II. It is also desirable in such systems that the unsaturated acids do not exceed about 15 percent by weight of the total acid and that preferably there are no conjugated or polyunsaturated acid molecules. The unsaturated acids should not contain more than one olefinic linkage, one example is oleic acid. Preferably the average carbon number in mixtures of the acids to be formulated as above is from 14 to 16, and the titre is from 35°C to 40°C.

In making soap the acids may be used as such, or in the form of salts other than soaps, fats, oils or esters.

For example when the fatty acids are in the form of free acids or esters, a neutralizing process or a saponifying process is employed in making soap. It is recognized that these and like processes are well known to those skilled in the art. The process for making soaps is determined by whether the acid of Formula II and unsaturated acid, such as oleic acid, to be mixed are free acids or esters.

In addition when the fatty acids are in the form of salts other than soaps, a conversion process is employed. In the neutralizing and saponifying process an alkali metal hydroxide may be used.

It is possible to further mix anionic surfactants such as higher alkyl sulphates, higher alkenyl sulfonates, polyoxy alkylene alkyl ether sulphates, polyoxyalkylene alkyl phenyl ether sulphates or alkyl aryl sulphonates and nonionic surfactants such as polyoxyalkylene alkyl ether, polyoxy alkyl phenyl ether or fatty acid esters of polyols in the neat soap to make it workable even in hard water, or to improve performance of the finished product. Neat soap made in accordance with the present invention is more stable than neat soap prepared with conventional unsaturated fatty acid formulations.

The neat soap can be made into solid soap by conventional methods such as with a frame process or a milling process and it can be moulded using known additives such as abrasive materials, inorganic or organic fillers, builders, superfatting materials, sequestrants or germicides according to the object. These fundamentals are well known to those skilled in the art.

Following is a description by way of example to further illustrate the compositions of the invention.

Example 1

The properties of soaps prepared experimentally using formulations similar to typical commercial toilet soap bars containing unsaturated fatty acid and no branched chain fatty acids were compared with experimentally prepared soaps containing branched chain fatty acids by employing the fatty acids with a purity of more than 90 percent.

The fatty acids neutralized with caustic soda (NaOH) by the conventional procedure were boiled and salted out to be finished. The neat soaps thus obtained were dried and moulded by a plodder after milling.

The oleic acid was obtained from partially hydrogenated tallow.

The branched chain fatty acids were a synthetic mixture with an average molecular weight of 280 having an alkyl radical in the α-position and having from 11 to 16 carbon atoms per molecule.

	Commercial Soap Type (Wt.)			*Product of the Present Invention (Wt.)*
	1	*2*	*3*	*4*
Compositions of fatty acids:				
Straight chain fatty acids	60	65	75	75
C_{12}	(10)	(10)	(10)	(10)
C_{14}	(5)	(5)	(30)	(30)
C_{16}	(25)	(25)	(25)	(25)
C_{18}	(20)	(25)	(10)	(10)
Unsaturated fatty acids	40	35	25	—
Oleic acid	(40)	(35)	(25)	
Branched chain saturated acids	—	—	—	25
Titre °C	38.6	41.9	37.6	37.4

Surface property of extruding moulded product		good	not so good	not so good	good
Solubility of abrasion* in 30 minutes in term of g/100 cm²					
	10°C	48.0	10.3	11.2	19.0
	40°C	147.1	128.6	104.8	148.0
Lather quickness (in numbers of strokes)*					
	10°C	31	122	more than 150	138
	40°C	14	19	26	24

* in above table the solubilities by abrasion were determined by the method described in Japanese Industrial Standard K-3304-1956 and the lather quickness are number of rubs of the soap until a certain amount of foaming was produced according to the method mentioned in J.Am.Oil Chemist Soc., *34* (2) 53 (1957).

The stabilities against rancidity of the above obtained sample 4, commercial toilet soap bar (A) similar to above sample (1) and (B) similar to above sample (2) were compared. Note that ordinary commercial soaps contain conjugated or poly-unsaturation in contrast to samples 1, 2, and 3 above. The absence of this in previous tests of samples 1, 2 and 3 was not significant for the present purposes.

	Commercial Soap A	*Commercial Soap B*	*Sample 4*
Appearance of discolouration	In 10 days	In 33 days	In 35 days
Appearance of rancidity odour	In 35 days	In 37 days	Stable for more than 50 days

Determination of discolouration and rancidity were carried out according to the method described in Monsanto Chemical Co.'s Technical Bulletin FC-3(1958), p.3.

The addition of some stabilizers are general practice in commercial soaps. The Sample 4 was stable without stabilizer.

Example 2

Solid soap was obtained by the same process described in Example 1 employing with oleic acid a mixture of synthesized branched chain saturated acids together with straight chain saturated acids (containing even number carbon chains and odd number carbon chains) having the following composition (1):

Mixed Synthetic fatty acids composition (1)

Straight chain saturated acids with even number carbon atoms chain

$C_{10}-C_{14}$	40.8 percent

Straight chain saturated acids with odd number carbon atoms chain

$C_{11}-C_{15}$	37.1 percent

Branched chain fatty acid with even or odd number of carbon atoms chain having mostly methyl radical branches

$C_{11}-C_{16}$		22.1 percent
Total	=	100.0 percent

Neutralization number	255.7
Ester number	1.3
Iodine number	0.08
Titer, °C	27.8

Fatty acids composition of the soaps:

Synthetic fatty acids (1 above)	85 parts (weight)
Oleic acid (iodine number 89)	15 parts
Surface property of extruding molded product with an extruder	good
Solubility by abrasion in 30 minutes; g/100 cm²:	
10°C	36.6
40°C	141.1

Lather quickens in numbers of strokes:

10°C	140
40°C	25

Example 3

The mixture of 40 percent myristic acid, 20 percent palmitic acid, 15 percent stearic acid, 10 percent α-butyl caprylic acid and 15 percent α-ethyl capric acid (percent in weight) was neutralized with aqueous caustic soda according to the conventional procedure to obtain a neat soap with a water content of about 30 percent. When the neat soap was dried in the form of chips then moulded by the milling soap process, solid soap with good plasticity was obtained.

Example 4

26 parts (active) of sodium lauryl sulfate, 2 parts of the sodium salt of sulfated lauroxy diethoxy ethanol and 2 parts of lauroyl monoethanolamide were mixed with 70 parts (weight) of the soap of the sample 4 described in Example 1, dyes and perfumes for toilet soaps were added thereto and the mixture was roll-milled, extruded through plodder and stamp-molded to obtain soap bars which can be used effectively even in hard water (300 ppm $CaCO_3$) at 40°C.

WHAT WE CLAIM IS:—

1. A composition for use in the manufacture of soap, which composition comprises a major amount of a mixture consisting of a major amount of an acid or acids having the formula

$$\text{II} \quad C_aH_{2a+1} - CH_2 - COOH$$

wherein a is an integer of from 9 to 20, and a minor amount of an acid or acids having the formula

$$\text{I} \quad C_nH_{2n+1} - \underset{\displaystyle C_mH_{2m+1}}{\underset{|}{CH}} - COOH$$

wherein n is an integer equal to or greater than 1, m is an integer equal to or greater than n, and the sum of m and n is greater than 8 but less than 25, the titre (melting point) of the mixture being from 35°C to 40°C.

2. A composition as claimed in claim 1, wherein the acid of Formula I is an α-methyl, α-ethyl, α-propyl or α-butyl acid.

3. A composition as claimed in claim 1 or claim 2, wherein the acid of Formula I is an α-substituted caproic, enanthic, caprylic, pelargonic, capric, undecanoic, lauric, tridecanic, myristic, pentadecanoic, palmitic, margaric, stearic, nonadecanoic or arachidic acid.

4. A composition as claimed in any one of the preceding claims, wherein the sum of m and n is greater than 10 but less than 19.

5. A composition as claimed in any one of the preceding claims, wherein the acid of Formula II is an acid of the coconut range of normal acids having from 8 to 16 carbon atoms per molecule, or stearic acid.

6. A composition as claimed in any one of the preceding claims, wherein the acid or acids of Formula II is or are present in an amount of up to 85% by weight of the mixture.

7. A composition as claimed in any one of the preceding claims, wherein the titre of the acid or acids of Formula I is approximately 14°C.

8. A composition as claimed in any one of the preceding claims, wherein the mixture comprises at least 15% of the acid or acids of Formula I.

9. A composition as claimed in claim 7 or claim 8, wherein the mixture comprises less than 30% of the acid or acids of Formula I.

10. A composition as claimed in any one of the preceding claims wherein there are present in the mixture 20 to 70 parts of the acid or acids of Formula I per 100 parts of the acid or acids of Formula II.

11. A composition as claimed in claim 10, wherein there are present 30 to 60 parts of the acid or acids of Formula I.

12. A composition as claimed in any one of the preceding claims which is free from straight chain unsaturated acids.

13. A composition as claimed in any one of claims 1 to 11 which includes a straight chain unsaturated acid or acids.

14. A composition as claimed in claim 13, wherein oleic acid is predominant in the unsaturated acid or acids.

15. A composition as claimed in claim 13 or claim 14, wherein there is present from 30 to 80 parts by weight of the acid or acids of Formula I and unsaturated acid or acids per 100 parts of the acid or acids of Formula II.

16. A composition as claimed in claim 15, wherein there is present from 50 to 70 parts by weight of the acid or acids of Formula I and unsaturated acid or acids.

17. A composition as claimed in any one of claims 13 to 16, wherein the unsaturated acid or acids does not exceed 15% by weight of the composition.

18. A composition as claimed in any one of claims 13 to 17, wherein the unsaturated acid or acids is free from conjugated and/or polyunsaturated acids.

19. A composition as claimed in any one of the preceding claims, wherein the average number of carbon atoms in the mixture is from 14 to 16.

20. A composition as claimed in any one of the preceding claims, wherein one or

more of the acids are present as a corresponding salt other than a soap, or an ester.

21. A soap when made from a composition as claimed in any one of claims 1 to 19 by neutralization.

22. A soap when made from a composition as claimed in claim 20 by saponification of the ester.

23. A soap when made from a composition as claimed in claim 20 by conversion of the salt.

24. A soap composition comprising a soap as claimed in any one of claims 21 to 23 in admixture with an anionic and/or non-ionic surfactant.

25. A soap composition as claimed in claim 24, wherein the anionic surfactant is a higher alkyl sulphate, a higher alkenyl sulphonate, a polyoxyalkylene alkyl ether sulphate, a polyoxyalkylene alkyl phenyl ether sulphate or an alkyl aryl sulphonate.

26. A soap composition as claimed in claim 24, wherein the non-ionic surfactant is a polyoxyalkylene alkyl ether, a polyoxy alkyl phenyl ether or a fatty acid ester of a polyol.

27. A soap composition comprising a soap as claimed in any one of claims 21 to 23 or a soap composition as claimed in any one of claims 24 to 26 in admixture with, as additives, one or more abrasive materials, inorganic or organic fillers, builders, superfatting materials, sequestrants, and/or germicides.

28. A soap or a soap composition when made from a composition as claimed in claim 1 and substantially as hereinbefore described with reference to any one of the specific Examples.

BOULT, WADE & TENNANT,
111 & 112, Hatton Garden,
London, E.C.2.
Chartered Patent Agents,

Agents for the Applicants.

Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd., Berwick-upon-Tweed, 1970
Published at the Patent Office, 25 Southampton Buildings, London WC2A 1AY from which copies may be obtained.